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Solvent issues during processing and device lifetime for perovskite solar cells

Peter J. Holliman*, Eurig W. Jones, Arthur Connell, Sanjay Ghosh, Leo Furnell and Robert J. Hobbs

This paper considers the manufacturing issues associated with dimethyl formamide, γ -butyrolactone, dimethyl sulfoxide and chlorobenzene solvents, in particular the health and safety issues of using these solvents in scaled perovskite photovoltaic processing. Issues of device lifetime are also considered, for example the effects of atmospheric conditions (e.g. humidity).

Keywords: Light harvesting, Photovoltaic, Manufacturing, Solvents, Hazards

Introduction

Perovskite solar cells are a new type of solid state photovoltaic (PV) device first reported by Snaith *et al.*¹. These devices use organo-lead(II) halide perovskite light harvesting pigments. These perovskite materials are generally based around a general formula RPbX_3 where R = a methylamine or a formamidinium cation and $\text{X} = \text{Cl}^-$, Br^- or I^- . This ionic versatility can be utilized. For instance, varying the halide anions gives rise to different pigment band gaps, device colours and efficiencies.² These devices are even more versatile because the perovskite light absorbers can also be deposited onto either planar metal oxide films;³ or onto TiO_2 or Al_2O_3 mesoporous scaffolds¹ (see Fig. 1).

Since Snaith's initial report of 12% efficient devices,¹ extremely rapid progress has been reported in improving device efficiencies. Many of these improvements have been focused around the processing of the perovskite absorber layer including $\eta = 15.9\%$ for solution-deposited perovskite⁴ and $\eta = 15.4\%$ for vapour-deposited perovskite.³ More recently, perovskite device efficiencies have reached almost 20% for lab-scale formamidinium lead iodide-based devices.⁵ This is comparable with the best 2nd-generation CdTe ⁶ and CIGS devices.⁷

Perovskite PV devices are also interesting because the organo-lead perovskite is able to simultaneously harvest light and to carry charge. This means that, in mesoporous devices, the metal oxide scaffold can be either TiO_2 or insulating Al_2O_3 . This is important because the potential to use different metal oxide scaffolds not only extends the range of possible scaffold materials, it also reduces the charge transport demands on the hole transport layer. Thus, because the perovskite carries charge, the hole transport material (HTM) does not need to be so effective in this regard. This limits the over-potential losses which occur for instance in dye-sensitized solar cells, giving rise to higher open-circuit voltages (V_{oc} ca. 1.0 V).

Given their recent discovery, a huge parameter space remains for perovskite devices. For instance, solvent-based processing of the organo-lead perovskites currently uses either dimethyl formamide (DMF)⁴, γ -butyrolactone (GBL)⁸ or dimethyl sulfoxide (DMSO).⁹ It is also known that DMF

solvent remains in the perovskite deposits after processing.¹⁰ The safety and toxicity issues associated with these types of solvents raise issues for scaling these devices. In addition, the most effective organo-lead halide perovskites are hygroscopic, which adds additional atmospheric management issues during manufacturing and also to the device and module encapsulation requirements.

This paper considers the manufacturing issues associated with DMF, GBL, DMSO and chlorobenzene (ClBz) solvents along with potential approaches towards perovskite processing which limit or eliminate the need for toxic solvents. The effects of atmospheric conditions (e.g. humidity) on perovskite device lifetimes are also considered.

Experimental

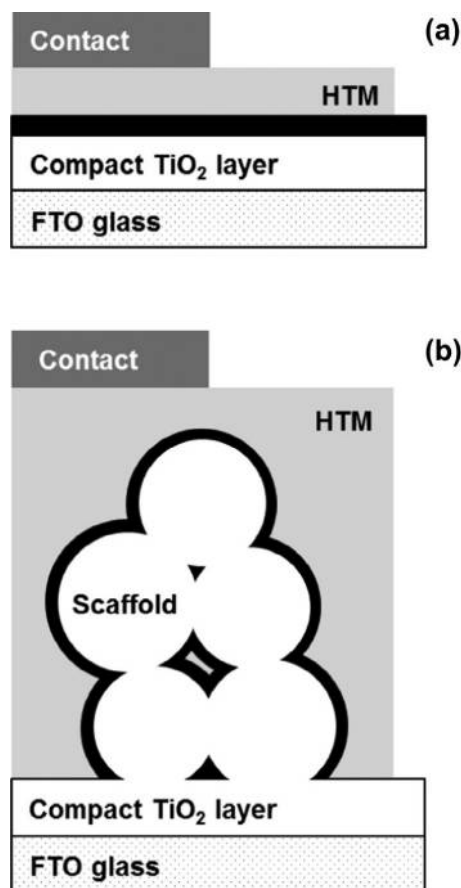
Perovskite precursors were prepared by reacting HX (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$) with excess methylamine (33 wt% in ethanol) at low %RH and at RT. Following this, solvent was removed *in vacuo* to induce precipitation of the methyl amine halide ($\text{CH}_3\text{NH}_3\text{X}$). The products were then dried to constant mass at 60 °C *in vacuo*.

Perovskite solutions were prepared by reacting lead(II) halide dissolved in DMF with methylamine halide ($\text{CH}_3\text{NH}_3\text{X}$) in a 1:3 stoichiometric ratio to give a 40% by weight concentration.

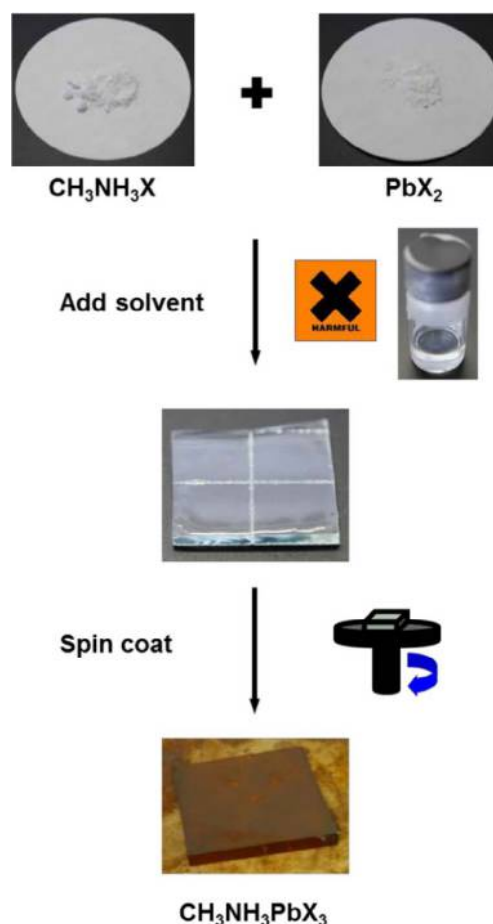
Devices were made (see Fig. 2) using pre-patterned fluoride-doped SnO_2 coated glass ($7 \Omega \square^{-1}$ FTO, TEC7, NSG) as the substrate. After thorough washing and drying under flowing N_2 , a thin, compact layer of TiO_2 was deposited by spin coating using a pre-made TiO_2 suspension (Solaronix) before heating to 550 °C for 60 min. In planar devices, perovskite precursor solution was spin coated directly onto this layer before heating to 100 °C. For mesoporous devices, a pre-made TiO_2 colloid (Dyesol AO paste) was diluted 1:3 w/w in ethanol and deposited by spin coating before sintering at 500 °C. A perovskite layer was then deposited by spin coating perovskite precursor solution before heating to 100 °C. A doped solution containing spiro-OMeTAD as a HTM was spin coated onto the perovskite layer (117 mM spiro-OMeTAD, 25 mM *tert*-butylpyridine, 10 mM lithium bis(trifluoromethylsulfonyl)imide salt) before contacting was completed using a metal evaporator.

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1 Schematic of *a* planar and *b* mesoporous perovskite devices (black layer denotes perovskite absorber in each case)



2 Schematic of the laboratory-scale manufacture of organo-lead halide perovskite films onto a glass substrate by precursor dissolution followed by spin coating

Results and discussion

As a potentially commercial PV technology, perovskite solar cells have a number of advantages. For instance, the device components should be relatively low cost once scaled up and the various device layers (Fig. 1) should in theory be printable onto flexible substrates (e.g. plastic, metal foil or ultra-thin glass). This combination of printability onto flexible materials makes roll-to-roll (R2R) processing a real possibility for this technology which, in turn, increases manufacturing throughput and reduces processing costs. However, perovskite R2R processing requires rapid, precise and conformal deposition of nano-scale device layers (Fig. 1) where each additional layer can be deposited onto the previous layer without damaging it.

In addition, when designing a R2R manufacturing line, the extra capital and running costs associated with vacuum processing generally make solution-based operations the preferred option (as long as this is possible for the chosen technology). Importantly, solution processing has been shown to be possible for lab-scale perovskite devices.

However, whilst effective solution processing of perovskite solar cells has been widely reported for lab-scale devices, there are still issues for scale-up. In particular, the dissolution of organo-lead precursors is very straightforward for organoamine halide salts (e.g. $\text{CH}_3\text{NH}_3\text{X}$) whereas lead(II) halides (i.e. PbX_2 where X = halide) is considerably more difficult and requires the use of one of a number of specialized solvents (e.g. DMF⁴ or GBL⁸ or DMSO⁹).

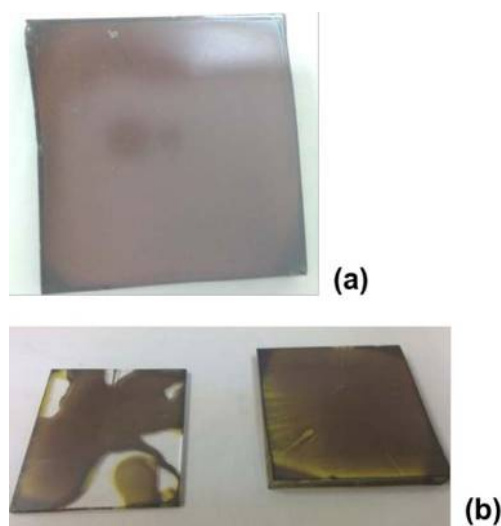
Table 1 shows selected parameters for these solvents mainly based around their vapourization, flammability and toxicity. In addition, these data should be considered within

a process temperature window of ambient to *ca.* 120 °C. Taking each solvent in turn and starting with DMF, this has a flashpoint of 67 °C and a boiling point of 153 °C so whilst its vapour pressure is low at 20 °C, it would be significant and potentially flammable at 100 °C. DMF is also classed as harmful and produces a number of acute and chronic toxicity responses.¹¹ As such it has a short-term exposure limit (STEL) of 30 mg m⁻³ (generally taken as 15 min exposure) and an 8-h time weighted average (TWA) limit of 15 mg m⁻³ characteristics. Hence, using DMF on a large scale would have serious health and safety implications. This is in part because DMF would be evaporated during processing but also because the resultant perovskite materials still contain significant amounts of DMF solvent.¹⁰ Thus, the continuous use of DMF solvent on a R2R line would require sophisticated vapour handling, recovery and scrubbing equipment which would significantly add to capital and operational costs. By comparison, whilst GBL has a higher b.p., it still has a flash point in the process temperature window and the highest v.p. at 20 °C of the three solvents studied. Whilst occupational exposure limits have not been set for GBL, it is known to cause serious eye damage and also to act as an anaesthetic and to cause depression because it acts as a dopamine suppressor.¹² DMSO, on the other hand, is not classed as toxic.¹³ However, it does have a flash point within the process temperature window and the lowest auto-ignition temperature of the three solvents (302 °C) suggesting flammability could be an issue. DMSO is also highly hygroscopic which could be a problem both during

Table 1 Selected properties of DMF, GBL, DMSO and ClBz

| | DMF ¹¹ | GBL ¹² | DMSO ¹³ | ClBz ¹⁴ |
|-------------------------------------------|----------------------------|-------------------|--------------------|--------------------|
| mp/°C | −61 | −45 | 16–19 | −45 |
| bp/°C | 153 | 204 | 189 | 132 |
| vp/mmHg | 2.7 | 15 | 0.42 | 11.8 |
| AIT/°C | 445 | 455 | 302 | 637 |
| FP | 67 | 98 | 95 | 27 |
| $\Delta H_{\text{vap}}/\text{kJmol}^{-1}$ | 42.3 | 52.2 | 47.3 | 41.0 |
| Water | Misc. | Misc. | Hygro-scopie | 0.2 g/L |
| OES/mg m ^{−3} | STEL 30 TWA 15 | NL | NL | 23 (4.6) |
| Hazard ID | Harmful irritant flammable | Harmful | Not toxic | Harm-ful |

Key shows: vp = Vapour pressure at 20 °C; AIT = Auto-ignition temperature; OES = Occupational exposure standard; FP = flashpoint; NL = no limit.



3 Photographs of *a* perovskite film as prepared and *b* perovskite films exposed to air for 2 h showing gradual colour change from black to yellow

manufacturing and after device production given the humidity damage which can occur during perovskite exposure. Finally, ClBz is also considered because this solvent is widely used to deposit spiro-OMeTaD onto the perovskite absorber layer. Whilst ClBz has a higher auto-ignition temperature than the other solvents it does have a much lower flash point at 27 °C. For the ClBz occupational exposure standards, whilst the STEL for ClBz is 70 mg m^{−3}, the TWA is 23 mg m^{−3}.

However, these are the EU values and the UK standards are much stricter (STEL = 13.8 mg m^{−3} TWA = 4.6 mg m^{−3}).

To consider what this means in reality, one could consider a situation where perovskite devices were being manufactured in a production facility with 1000 m³ of air space (e.g. 50-m long by 10-m wide by 2.5-m tall and containing 250 m³ of production equipment). For DMF, this would mean that a solvent volume of 16 ml vaporized into static air would reach the TWA limit. For ClBz, using the UK limit, only 4.2 ml would need to be vaporized to reach the TWA OES. This suggests that, either substantial atmospheric control would be required and/or that there is an urgent need to identify alternative solvents for perovskite device processing.

In addition to these manufacturing considerations, whilst a great deal of academic time in PV research is spent on optimizing PV device efficiencies, device lifetimes are at least as important an issue for commercial modules. Device lifetimes are important because the first and minimum target for any PV technology must be for it to reach its payback time both in terms of its embodied energy (i.e. the energy required to make the

device) and the system installation costs. Whilst it is estimated that perovskite PV should be affordable and so payback times should be relatively short, it is also known that, for perovskite PV, high humidity during manufacturing has a significant negative influence on device performance.¹⁵ However, humidity is also suspected to be an important factor in perovskite device failure with time. For example, Fig. 3 shows photographs of a film of CH₃NH₃PbX₃ deposited on a glass substrate and exposed to air. The data show that the material gradually and inhomogeneously changes colour from dark grey/black to bright yellow with time. This process initially takes place at the edges of the film and gradually works inwards until the entire film has changed colour. Interestingly, our data also suggest that this process can be reversed if the film is re-heated quite soon after the yellow colour is observed. However, it also appears that, if the film is left too long, the change appears to become permanent. We are currently studying this process in greater detail to understand the reasons behind the reversibility of this colour change and what this might mean for perovskite devices during ‘real life’ testing.

Conclusion

Perovskite solar cells represent a huge opportunity for large-scale, affordable 3rd-generation solar energy. Key to achieving this is to control each manufacturing step to ensure that the rapid lab-scale advances being made can be transferred to module-sized devices. In this context, when designing a manufacturing process, the materials sets can vary but decisions on processing approaches need to be made in advance (e.g. solvent or vacuum processing). This paper considers solvent-based approaches; the issues of solvent choice and its implications for manufacturing lines and device lifetime. Our analyses suggest that there is an urgent need to consider other solvents or solvent-free processes to (i) reduce the need for solvent handling/recovery during manufacturing and (ii) residual solvent in the perovskite absorber materials.

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